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MODELLING DIRECTIONAL SOLIDIFICATION

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SUMMARY

Objective

This grant is a continuation of Contract NAS8-34891. The overall objective of this program is to develop an improved understanding of phenomena of importance to directional solidification, to enable explanation and prediction of differences in behavior between solidification on Earth and in space. Currently emphasis is on determining the influence of convection and freezing rate fluctuations on compositional homogeneity and crystalline perfection.

Progress

This is a combined second and third semi-annual report, i.e. an annual report. Below is a summary of progress made this last year. Details follow.

Significant personnel changes have occurred since the first semi-annual report one year ago. Lorraine Ruggiano resigned shortly after the last report was written to take employment in industry. In June a new student, Ross Gray, was recruited to replace her. Greg Neugebauer successfully defended his M.S. thesis on April 18, 1986 and passed his Ph.D. qualifying examination on August 15, 1986. The research proposition for his Ph.D. qualifying exam is included here as Appendix F. In January of this year a new Ph.D. student, Mohsen Banan, joined us after completing his M.S. in physics under Professor Lal at the A & M University of Alabama.

The following four papers were published this last year and are included here as Appendices A through D.

1. H. Potts and W.R. Wilcox, "Chaotic Asymmetric Convection in the Bridgman - Stockbarger Technique," J. Crystal Growth 74, 443 (1986). (Appendix A.)

2. R. Sen and W.R. Wilcox, "Behavior of a Non-wetting Melt in Free Fall: Experimental," J. Crystal Growth 74, 591 (1986). (Appendix B.)

3. R. Sen and W.R. Wilcox, "Behavior of a Non-wetting Melt in Free Fall: Theoretical," J. Crystal Growth 78, 129 (1986). (Appendix C.)

4. R. Sen and W.R. Wilcox, "Twinning of Dodecanedicarboxylic Acid," J. Crystal Growth 75, 323 (1986). (Appendix D.)

From Greg Neugebauer's M.S. thesis the following paper was written and submitted for publication to the Journal of Crystal Growth. It is included here as Appendix E.

G.T. Neugebauer and W.R. Wilcox, "Convection in the Vertical Bridgman-Stockbarger Technique," submitted to J.

Crystal Growth.

The following ten presentations were made at meetings, conferences and seminars:

1. G.T. Neugebauer and W.R. Wilcox, "Convection in the Vertical Bridgman-Stockbarger Technique;"

   a. A & M University of Alabama (Huntsville, December 1985; not included in last report).

   b. New England Section of the American Association for Crystal Growth (New Jersey, April 1986).

   c. Bulgarian Academy of Science (Sofia, June 1986).

   d. International Conference on Crystal Growth - 7 (York, England, July 1986).

   e. American Conference for Crystal Growth / East - 1 (Atlantic City, October 1986).

   f. Center for Advanced Materials Processing (Potsdam, New York, October 1986).

   g. Univerity of Colorado (Boulder, February 1987).

2. W.R. Wilcox and R. Sen, "Behavior of a Non-Wetted Melt in Free Fall;"

   a. TMS AIME Meeting (New Orleans, March 1986).

   b. International Conference on Crystal Growth - 7 (York, England, July 1986).

3. W.R. Wilcox, "Validity of the Burton-Prim-Slichter Equation," International Conference on Crystal Growth - 7 (York, England, July 1986).

Greg Neugebauer added a short heater to the top of his old Bridgman - Stockbarger apparatus and demonstrated that buoyancy-driven free convection can be made unobservable by causing the temperature to increase with height throughout the molten organic. A new apparatus was constructed to permit solidification to take place with control of the free convection. The objective is to determine the influence of convection on doping homogeneity using transparent organic compounds as models of technologically important materials. Preliminary experiments with naphthalene as a host material revealed problems with bubble formation and native impurities.

Ross Gray conducted a literature review on solidification of concentrated semiconductor alloys. He constructed a vertical Bridgman

- Stockbarger apparatus for solidification of indium gallium antimonide with spin-up / spin-down (accelerated crucible rotation technique). The objective is to determine the influence of forced convection on compositional homogeneity and crystallographic perfection. In a different NASA project another graduate student, Mark Larrousse, found that spin-up / spin-down causes a large fluctuation in mass transfer rate. This would be expected to generate serious compositional fluctuations during directional solidification. However such striations would be very close together for the slow freezing rates necessary in the solidification of concentrated alloys in order to avoid constitutional supercooling. During cooldown after solidification it might be expected that solid state diffusion would cause these striations to decay. Ross Gray and Mark Larrousse have been collaborating on a theoretical treatment of the diffusional decay of compositional striations during growth. They found that decay increases as the frequency of striation generation increases, the freezing rate decreases, the temperature gradient in the solid decreases, and as the diffusion coefficient in the solid increases.

Mohsen Banan will determine the influence of freezing rate oscillations on the compositional homogeneity and perfection of indium gallium antimonide. The oscillations will be generated by imposing an alternating electric current along the length of the sample during solidification. He has begun a literature review and design of his apparatus.

Plans

Following is the work planned for the next six months.

Greg Neugebauer will develop techniques for solidifying naphthalene without bubbles, with controlled impurity content, and of large grain size without interface breakdown. He will also develop techniques for sectioning solidified naphthalene and for determining the anthracene concentration vs. position. Ross Gray will complete the theoretical study of diffusional decay of striations, providing guidance on when near-total decay is to be expected. He will write a paper for publication. He will perform preliminary solidification runs on his apparatus. He will prepare a research proposition and take his Ph.D. qualifying examination.

Mohsen Banan will construct his apparatus and perform preliminary experiments. He will prepare a research proposition and take his Ph.D. qualifying examination.

INFLUENCE OF SPIN-UP/SPIN-DOWN ON COMPOSITIONAL HOMOGENEITY AND PERFECTION OF DIRECTIONALLY SOLIDIFIED INDIUM GALLIUM ANTIMONIDE

Ross Gray

Summary

One objective of this project is to determine the effect of spin-up / spin-down (accelerated crucible rotation technique; ACRT) on the radial and axial compositional homogeneity of $In_xGa_{1-x}Sb$ solidified from the melt by the vertical Bridgman-Stockbarger (VBS) technique. A related objective is to determine the effect of ACRT on the formation of grain and twin boundaries in this alloy. The effects of ACRT will be studied vs. composition of the alloy, freezing rate, and rotation rate.

The VBS growth apparatus was designed, constructed and debugged. It includes a furnace (1000°C maximum) on top of a water-jacketed copper cooler. The heater and cooler are separated by a layer of insulation. The apparatus utilizes a translation unit to move the growth ampoule through the heater - insulator - cooler at a steady controlled rate, a gearmotor to rotate the ampoule about its axis, a temperature controller for the heater, and a cooling and circulating bath to pump antifreeze through the cooler.

A theoretical model was developed for the effects of solid state diffusion on compositional striations in a growing crystal. (Striations are expected to be generated by the fluctuations in heat and mass transfer at the growth interface caused by ACRT.) It was found that any striations generated by ACRT during solidification of $In_xGa_{1-x}Sb$ should decay long before room temperature is reached.

Background and Introduction

Bulk crystals of $In_xGa_{1-x}Sb$ have possible applications as photodetectors, light-emitting diodes, and lasers (1,2,3). Such alloys offer the advantage of composition-dependent properties, which allows one to select properties to suit different applications. The optimum composition for the devices above is about 80% GaSb.

For bulk applications, homogeneous single crystals with low defect densities are required. However, this is very difficult to achieve, especially in alloy systems where extensive segregation is a problem. For example, as $In_xGa_{1-x}Sb$ solidifies InSb is rejected from the solid. When combined with convection this leads to axial and cross-sectional variations in composition.

Constitutional supercooling (4,5,6) is also a serious problem in solidification of concentrated alloys. A schematic diagram of constitutional supercooling is shown in Figure 1. It leads to

breakdown of a planar growth interface to a cellular one, with accumulation of rejected solute in the cell boundaries. New grains and possibly twins are formed. If constitutional supercooling is severe, dendritic growth results. For concentrated alloys a high temperature gradient at the interface in conjunction with a steady low growth rate are required to avoid morphological instability.

Natural convection resulting from composition and/or temperature variations in the melt is often present during growth in a gravitational field. This convection is often time-dependent (7), causing variations in temperature and flow velocity near the interface. The consequences are growth rate fluctuations, compositional striations and, in the case of concentrated alloys, transient constitutional supercooling and possibly generation of grains and twins.

It is a fact that growth of concentrated semiconductor alloys on Earth is plagued by compositional inhomogeneities, small grain size, and twins. The causes are not certain, but are suspected to be related to gravity.

The problems arising from gravity have been investigated by growing $In_xGa_{1-x}Sb$ in space (8,9,10,11). The reduced gravitational field present in space allows one to practically eliminate buoyancy-driven convection. Wilcox et al.(9) found that ingots of $In_xGa_{1-x}Sb$ grown in space by the gradient freeze method exhibited much less twinning than ingots grown on earth under otherwise identical conditions. One proposal is that the growth rate fluctuates on Earth, causing constitutional supercooling to occur so rapidly that the interface does not have time to form cells. Twins and grains nucleate instead. Another proposal is that twins and grains are nucleated by foreign particles contacting the growing interface, and that this contact is much more frequent with gravity causing the particles to settle and causing convection which moves the particles along the interface (10).

Sen (12) applied a transverse magnetic field to reduce convection when growing $In_xGa_{1-x}Sb$ by the vertical Bridgman-Stockbarger(VBS) technique. She found that application of the field considerably reduced the number of grain and twin boundaries. The magnetic field also caused a slight radial variation in composition.

Elimination of natural convection is not the only way to relieve the problems caused by time-dependent flow and temperature at the interface. Forced convection can be introduced on a scale that will overwhelm any natural convective effects. Using forced convection offers the advantage of keeping the melt well-mixed and, coincidentally, eliminating the effects of a non-axisymmetric furnace. The major obstacle to achieving stirring evolves from the inability to place a mechanical stirring device inside the growth ampoule. A stirrer could be a source of impurities. Generally a semiconductor must be totally sealed in an inert atmosphere to prevent escape of volatile components and to keep the melt from reacting with the ambient atmosphere. Spin-up / spin-down, often called the accelerated

crucible rotation technique (ACRT), is a method by which effective mixing can be achieved without inserting a stirring device. The entire ampoule is rotated about its axis for a short period of time (spin-up), motion is stopped for another short period (spin-down), and this cycle is continuously repeated.

Horowitz et al. (13) applied ACRT to the Bridgman growth of incongruently melting Rb_2MnCl_4 from non-stoichiometric melts. They found that ACRT allowed the maximum growth rate yielding inclusion-free crystals to be increased by at least a factor of four. Scheil (14) applied ACRT to the high-temperature flux growth of $GdAlO_3$ from PbO-PbF_2-B_2O_3 solutions. He noted that ACRT permitted much higher crystal growth velocities. ACRT was also used by Capper et al. (15) to grow $Cd_xHg_{1-x}Te$ by the Bridgman technique. This resulted in ingots with greatly improved radial compositional homogeneity. In addition, ingots grown with ACRT had many fewer and consequently larger major grains. They speculated that this was due to the vigorous convection scrubbing newly nucleated crystals from the ampoule wall before they could be incorporated by the solidification front. (Based on the results of Mark Larrousse at Clarkson, showing large fluctuations in transport during each spin-up / spin-down cycle, it is suggested that grain selection might be enhanced by alternating growth with melt-back.)

The objective of this project is to determine the effects of ACRT on the radial and axial compositional homogeneity of $In_xGa_{1-x}Sb$ grown by the VBS technique. The effect of ACRT on twin and grain boundary formation will also be determined. The knowledge gained by determining these effects can then be used to help in understanding the growth of alloy systems from the melt.

Progress

This year's accomplishments were:

1. Designed VBS apparatus.
2. Purchased necessary equipment and materials.
3. Assembled and debugged VBS apparatus.
4. With Mark Larrouse created theoretical model of diffusional decay of striations during growth.
5. Ran computations for striation decay under a variety of conditions.

The furnace necessary for the VBS growth of $In_xGa_{1-x}Sb$ was designed and assembled as shown in Figure 2. The heating element consists of a 12 inch coil of Kanthal wire with an ID of 3 inches, surrounded by Fibrothal insulation of 9 inch OD. This was purchased from the Kanthal Corporation of Bethel, CT. The ends of this cylindrical heating element are covered by two 1/2 inch thick, cylindrical, 12 inch OD pieces of ZYZ-6 zirconia insulation. These insulating disks were purchased from Zircar Products, Inc., Florida, NY. The purpose

of the insulating region between the heater and cooler is to insure a more planar interface during growth (16). The insulation also reduces the sensitivity of the interface shape to changes in operating conditions.

A small 15mm ID by 20mm OD quartz tube is used as a furnace liner and is held in place by the zirconia insulation. This tube, along with 9mm ID by 11mm OD quartz tubes for growth ampoules, were purchased from Quartz Scientific, Inc. of Fairport Harbor, Ohio. A 1/4 inch thick, 12 inch OD copper plate sits on top of the furnace for mechanical stability. The cooler was constructed from two of these copper disks separated by two concentric copper pipes which serve as a heat exchanger, through which antifreeze is passed. The furnace is enclosed in a 0.016 inch thick piece of aluminum sheet metal. The control of the temperature in the furnace is achieved by a model 6001K microprocessor-based controller manufactured by Omega Engineering, Inc. of Stamford, CT. This is an on-off controller with a PID algorithm that outputs a 120 V signal. Since the Kanthal heating element can operate at 60 V maximum, the signal from the controller is sent to a model 126 Powerstat variable autotransformer, where it can be stepped down to the necessary voltage. The input signal to the controller is supplied by an inconel-sheathed, K-type thermocouple inserted into the furnace as shown in Figure 2. All temperature measuring devices were purchased from Omega Engineering, Inc. The controller was properly tuned and the variable transformer adjusted so that the temperature in the heater could be maintained to plus or minus $1^{o}C$. Additional holes were made through the top pieces of copper and insulation on the furnace to allow for the insertion of three more thermocouples. This is to allow for the measurement of furnace temperature at various radial and axial positions in the furnace. These thermocouples are connected to a rotary switch which allows the output of any thermocouple to be read by a model 660 digital thermometer. The cooling is provided by circulating a 50-50 mixture of antifreeze and water through the cooler. This is accomplished by a model RC-6 Lauda Circulator, manufactured by Brinkmann Instruments, Inc. of Westbury, NY. This provides temperature control of plus or minus $0.1^{o}C$.

In VBS growth, a motion mechanism is necessary to lower the sealed growth ampoule down the temperature gradient supplied by the heater - insulator - cooler combination. Extremely slow translation rates (about 4mm/day) are necessary to avoid constitutional supercooling in this material. A model 202 zone refiner was purchased from Crystal Specialties, Inc. of Portland, OR. This was modified to stand in an upright position and to give the desired translation rates. A Bodine NSH-12R gearmotor was mounted on the zone refiner to rotate the ampoule. This motor is controlled by a Minarik SL15 controller which is plugged into a GraLab 625 timer. This allows the ACRT cycle times to be programmed. A 1/2 inch drill chuck was modified and placed onto the gearmotor to hold the ampoule. A block diagram of the basic experimental setup is shown in Figure 3.

The gallium, indium, and antimony were purchased in 1/8 inch shot form. 150g of gallium(69s) and 400g of antimony(69s) were purchased

from Cerac, Inc. of Milwaukee, WI. 100g of indium was purchased from GFS Chemicals, Columbus, OH.

In recent experiments at Clarkson, Mark Larrousse found that ACRT produces large fluctuations in the mass transfer rate at the melt-solid interface (17). This implies that the composition of impurity in the grown solid would also fluctuate, producing striations. However, the high temperature present in the solid near the interface could cause these striations to damp out and never be seen. In order to determine if striations would be frozen into a grown ingot, a one-dimensional, time-dependent model was developed (18).

The model was developed by considering a volume element of differential thickness and unit area in a solidifying ingot, as shown in Figure 4. A material balance around this element gives:

$$\frac{\partial}{\partial x}\left(D\,\frac{\partial C}{\partial x}\right) - V\,\frac{\partial C}{\partial x} = \frac{\partial C}{\partial t} \qquad (1)$$

where $$D = D_o \exp\left[-\frac{Q}{R(T_m - Gx)}\right] \qquad (2)$$

D_o is the diffusion pre-exponential, Q is the activation energy for diffusion, T_m is the equilibrium melting temperature of the solid, G is the temperature gradient in the solid, x is the distance into the ingot from the freezing interface, C is concentration, R is the gas constant, t is time, and V is the crystal growth rate. The diffusivity D varies exponentially with inverse temperature T and, consequently, varies markedly with distance x along the ingot. The temperature gradient G in the solid is assumed to be constant.

The boundary conditions are:

$$C(0,t) = C_o + A\,\sin\left(\frac{2\pi}{t_c}\,t\right) \qquad (3)$$

$$C(\infty,t) = \text{BOUNDED}, \qquad (4)$$

$$C(x,0) = C_o \qquad (5)$$

where t_c is the ACRT cycle time, A is the amplitude of the composition variations in the solid at the freezing interface, and C_o is the initial concentration throughout the solid (assumed constant).

These equations were non-dimensionalized by the following definitions:

$$\bar{C} = \frac{C - C_o}{A}, \quad \bar{x} = \frac{x}{Vt_c}, \quad \bar{t} = \frac{D_o}{t_c{}^2 V^2 t} \qquad (6)$$

with the bars denoting dimensionless quantities. The boundary conditions become thereby:

$$\bar{C}(0,\bar{t}) = \sin\left[\frac{2\pi t_c v^2}{D_o}\bar{t}\right] \tag{7}$$

$$\bar{C}(\infty,\bar{t}) = \text{BOUNDED} \tag{8}$$

$$\bar{C}(\bar{x},0) = 0 \tag{9}$$

The essential assumptions in the model are:

1. One dimensional (i.e. a planar interface).
2. Constant temperature gradient G.
3. Constant growth rate V.
4. Semi-infinite ingot.
5. Sinusoidal variation in composition at the interface.

This model was solved by a finite-difference method on the Z-200 microcomputer. The results for conditions which simulate $In_xGa_{1-x}Sb$ solidification are shown in Figure 5 for a dimensionless time of 600. This is a time sufficient for six full cycles to have grown in. It can be seen that all striations, except for the first peak, decay within 3 wavelengths of the interface. This corresponds to a distance of only 8.3 micrometers. The first peak is slow to decay because it suffers from a lack of driving force on its right-hand side; it is the only maximum that does not have minima on both sides. The fast decay of striations suggests that they will not be observable in the high-temperature melt growth of $In_xGa_{1-x}Sb$ alloys using ACRT.

Low growth rates and large temperature gradients are necessary to prevent constitutional supercooling in alloys with a large concentration difference between the melt and the solid in equilibrium with it. These conditions cuase the solid to remain at an elevated temperature for a long time, promoting diffusion.

It has also been suggested that striations may be caused by g-jitter present in spacecraft. This model suggests that any striations caused by such high frequency oscillations would be damped quickly.

Computations have been carried out with other ACRT cycle times and diffusion coefficients.

Plans

In the next six months the following will be done:

1. Complete the theoretical study of diffusional decay of striations, providing guidance on when near-total decay is to be expected. A paper will be written for publication.